SUPPORTING INFORMATION

MANUSCRIPT TITLE: *Influence of Chelating Agents on Biogenic Uraninite Reoxidation by Fe(III) (hydr)oxides*

AUTHOR NAMES: Brandy D. Stewart[1], Crystal Girardot[1], Nicolas Spycher[2], Rajesh K. Sani[3], and Brent M. Peyton[1]

AUTHOR ADDRESS: [1]Chemical and Biological Engineering, Montana State University, Bozeman, MT 59717; [2]Lawrence Berkeley National Laboratory, Earth Sciences Division [3]South Dakota School of Mines and Technology, Chemical and Biological Engineering Department

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Materials and Methods

Dissolution Experiments. Iron dissolution experiments investigated the effect of various chelators (citrate, DFB, NTA, and EDTA) on solubilization of Fe(III) (hydr)oxides. Batch experiments were conducted with 100 mL of 10 mM PIPES (1,4-Piperazinediethanesulfonic acid) buffer at pH 7. Experiments also contained 2 g iron-coated sand (approximately 2.5 mM Fe(III) in each system) and a chelator concentration of 0 mM (control), 0.1 mM, or 0.2 mM. Experiments were conducted for approximately 80 d. Samples were filtered through 0.2 μm filters and stored in 5% HNO_3 at 4 °C until ICP-MS analysis for Fe. Separate experiments were run for each of the three Fe(III) (hydr)oxides tested (ferrihydrite, goethite, and hematite) as well as each chelator (DFB, citrate, EDTA, and NTA). Systems with all chelators were investigated in the absence of bicarbonate. Additionally the impact of bicarbonate on the solubilization of Fe(III) in the presence of NTA and EDTA was examined by adding 10mM potassium bicarbonate to these systems. Experiments were conducted in triplicate and are reported as the average +/- standard deviation.

Results and Discussion

Dissolution Experiments. The ability of EDTA, NTA, and citrate to solubilize ferrihydrite, goethite, or hematite was investigated in a series of batch experiments with 0 mM (all chelators) or 10 mM (only EDTA and NTA) bicarbonate at pH 7. Production of soluble Fe was most extensive with EDTA in the presence or absence of bicarbonate; however, NTA and citrate also increased Fe dissolution rates to a lesser extent. EDTA

was the most effective at solubilizing the Fe(III) (hydr)oxides. As shown in Table S1, dissolution rates were dependent on the EDTA concentration with the highest initial rate of 8.6 μM Fe d^{-1} with ferrihydrite and 0.2 mM EDTA. NTA solubilized ferrihydrite at an initial rate of 1.1 μM Fe d^{-1} with 0.2 mM NTA. Citrate was the least effective in solubilizing the Fe(III) (hydr)oxide minerals with the highest rate of 0.2 μM Fe d^{-1} measured for ferrihydrite and 0.2 mM citrate (Table S1). These results follow the thermodynamic stability constants (log K) for Fe(III) (Table S2) with EDTA having the largest stability constant, then NTA, and citrate having the lowest (log K = 25.1, 16, and 11.19, respectively) ((1)).

Of the Fe(III) (hydr)oxides studied, ferrihydrite was the most reactive followed by hematite, then goethite. NTA and citrate promoted dissolution of ferrihydrite; however, very little dissolved Fe was detected in systems with goethite or hematite and initial rates were below 0.29 μM Fe d^{-1} (Table S1). When compared to EDTA, NTA was not as efficient in the solubilization of ferrihydrite, as NTA binds to iron with a lower stability constant than EDTA. There was virtually no difference with the addition of 10 mM bicarbonate to the rate and extent of Fe(III) (hydr)oxide promoted dissolution with EDTA and NTA.
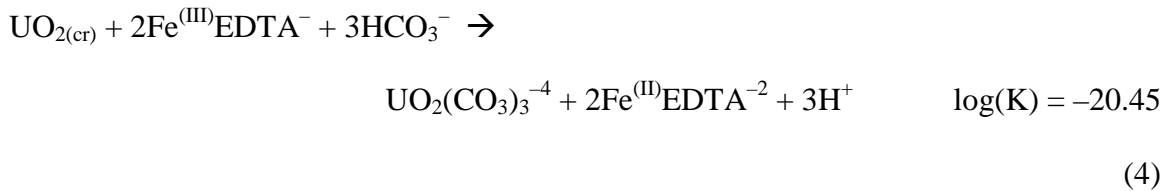
Thermodynamic analysis.

The reoxidation of uraninite in the presence of Fe(III) (hydr)oxides and chelators was evaluated by geochemical modeling using the program TOUGHREACT (Xu et al., 2011) and available thermodynamic data from the literature. For inorganic species, the same stability constants (log(K) values) as those reviewed by Spycher et al. (2011) were

selected, mostly from SNL (2007) and including data from Guillaumont et al. (2003) for uranium species. For chelated species, stability constants were taken from various literature sources, including data for U(IV), U(VI), Fe(II) and Fe(III) chelates reported by Hummel et al. (2005), Bonin et al. (2008 and 2009) and deStefano et al. (2006) (Table S2). It should be noted that the stoichiometry and stability constants of some of these chelated species vary from one data source to another. A complete re-evaluation of available thermodynamic data for chelated species was beyond the scope of this study, however an effort was made to select data from reputable sources and insure some degree of consistency with other thermodynamic data included in the analyses. It should be noted that Kantar et al. (2005) reported an alternative data set for uranyl citrate species, including combined Fe-uranyl-citrate species. Because data for such combined species were not found for the other chelators, nor included in the NEA compilation by Hummel et al. (2005), thermodynamic analyses using such combined species were not reported here. Nevertheless, analyses using the alternative data set of Kantar et al. (2005) for the citrate system were conducted and showed results similar to those presented here. In any case, the results of thermodynamic analyses presented here should be considered more qualitative than quantitative.

The modeling approach consists in simulating the reaction (at equilibrium) of Fe(III) (hydr)oxide (as either $Fe_2O_{3(cr)}$ or $Fe(OH)_{3(am)}$) and uraninite (as $UO_{2(cr)}$) over a range of pH (5 to 9), starting with an initially fully reduced system (pe < -5) in a fashion similar to that reported by Spycher et al. (2011) for a similar system without chelators. Meta-schoepite and siderite are also allowed to precipitate but do not form in the present case. The system contains 0.2mM of chelator (citrate, NTA or EDTA), 10 mM $KHCO_3$

and a non-limiting supply of solids reflecting experimental conditions. Crystalline UO_2 was preferred in this analysis because the thermodynamic data for this phase is better constrained than for nanoparticulate biogenic UO_2. It should be noted that simulations using biogenic UO_2 (as amorphous UO_2, Guillaumont, 2003) were also carried out, but yielded dissolved uranium concentrations much higher than experimental values. It is not known if this reflects the high uncertainty of biogenic UO_2 solubility (Ulrich et al., 2008; Spycher et al., 2011), the possibility of surface passivation and/or increased aggregation/ripening in the presence of chelators, or simply that the washing of the biogenic UO_2 (Materials and methods) prior to the experiments eliminated the smallest and most reactive UO_2 particles. *Please refer to manuscript body for initial discussion and governing equations.*

At pH below about 6.5, and only in the citrate system, reoxidation is further driven by the formation of a uranyl-citrate species ($UO_2Citrate^-$). Similar chelated uranyl species are not predicted to form in significant amounts (relative to carbonate species) in either the NTA or EDTA systems. In the EDTA system, the formation of strong Fe(III)-EDTA complexes at pH < ~7 hinder the reoxidation of UO_2 by tying up soluble Fe(III), resulting in about one order-of-magnitude lower uranium solubility at pH 5.5 than at pH 7 (Figure 7):

$$UO_{2(cr)} + 2Fe^{(III)}EDTA^- + 3HCO_3^- \rightarrow$$

$$UO_2(CO_3)_3^{-4} + 2Fe^{(II)}EDTA^{-2} + 3H^+ \qquad \log(K) = -20.45$$

(4)

It should be noted that in the EDTA case, all EDTA in the system (0.2 mM) is tied to either Fe(III) (at pH < 7) or Fe(II) (at pH > 7). Also, in all systems, the computed

concentrations of chelated U(IV) species are insignificant and fall below the range of concentrations shown on Figure 7.

Computed total U and Fe dissolved concentrations for systems containing ferrihydrite instead of hematite are also shown on Figure 7. Speciation results in this case (not shown) are similar to the hematite case, with significantly higher computed concentrations of dissolved species (more reoxidation) because of the higher solubility of ferrihydrite compared to that of hematite (Table S2). In the EDTA system, at pH > 6, the total dissolved Fe and U concentrations for systems with either hematite, goethite, or ferrihydrite are essentially the same because soluble Fe is limited by the amount of available EDTA. Only in the ferrihydrite system, below pH ~6, the computed total dissolved Fe and U concentrations increase with decreasing pH because $Fe(II)_{aq}$ becomes dominant over chelated Fe(III). These simulations illustrate the complex speciation in these systems and strong influence of pH on both redox state and the amount of Fe and U in solution.

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Table S1. Average initial rates for Fe(III) (hydr)oxide dissolution experiments with ferrihydrite (Ferri), goethite (Goe), or hematite (Hem) with 0 mM chelator (EDTA, NTA, or citrate (cit)), 0.1 mM chelator, or 0.2 mM chelator in the presence of 0 or 10 mM bicarbonate.

	Ave. Initial Rate (μM Fe d^{-1})		Ave. Initial Rate (μM Fe d^{-1})
Ferri + 0Chelator + 0Bi	0.0E+00	Goe + 0.1NTA + 0Bi	0.0E+00
Ferri + 0Chelator + 10Bi	2.1E-02	Goe + 0.1NTA + 10Bi	1.9E-02
Ferri + 0.1EDTA + 0Bi	4.2E+00	Goe + 0.2NTA + 0Bi	1.3E-02
Ferri + 0.1EDTA + 10Bi	4.2E+00	Goe + 0.2NTA + 10Bi	2.6E-02
Ferri + 0.2EDTA + 0Bi	8.6E+00	Goe + 0.1Cit + 0Bi	8.5E-02
Ferri + 0.2EDTA + 10Bi	8.3E+00	Goe + 0.2Cit + 0Bi	1.5E-01
Ferri + 0.1NTA + 0Bi	2.8E-01	Hem + 0Chelator + 0Bi	0.0E+00
Ferri + 0.1NTA + 10Bi	3.7E-01	Hem + 0Chelator + 10Bi	1.6E-02
Ferri + 0.2NTA + 0Bi	1.1E+00	Hem + 0.1EDTA + 0Bi	4.2E+00
Ferri + 0.2NTA + 10Bi	9.1E-01	Hem + 0.1EDTA + 10Bi	1.7E+00
Ferri + 0.1Cit + 0Bi	6.5E-03	Hem + 0.2EDTA + 0Bi	6.4E+00
Ferri + 0.2Cit + 0Bi	2.0E-01	Hem + 0.2EDTA + 10Bi	2.3E+00
Goe + 0Chelator + 0Bi	1.4E-02	Hem + 0.1NTA + 0Bi	6.9E-03
Goe + 0Chelator + 10Bi	0.0E+00	Hem + 0.1NTA + 10Bi	2.3E-02
Goe + 0.1EDTA + 0Bi	1.6E+00	Hem + 0.2NTA + 0Bi	2.5E-02
Goe + 0.1EDTA + 10Bi	5.9E-01	Hem + 0.2NTA + 10Bi	2.9E-02
Goe + 0.2EDTA + 0Bi	1.9E+00	Hem + 0.1Cit + 0Bi	2.8E-01
Goe + 0.2EDTA + 10Bi	6.9E-01	Hem + 0.2Cit + 0Bi	2.9E-01

Table S2. Subset of thermodynamic data and sources used in the thermodynamic analyses

Species	Log(K)	Stoichiometric coefficients in reaction (Negative for reactants, positive for products)												ref
		H_2O	H^+	Fe^{+2}	Fe^{+3}	U^{+4}	UO_2^{+2}	K^+	Citrate^{-3}	NTA^{-3}	EDTA^{-4}	CO_3^{-2}	e^-	
H(citrate)$^{-2}$	-6.40		1						1					a
H$_2$(citrate)$^-$	-11.16		2						1					a
H$_3$(citrate)$_{(aq)}$	-14.29		3						1					a
Fe(citrate)$^-$	-6.10			1					1					a
FeH(citrate)$_{(aq)}$	-10.20		1	1					1					a
Fe(citrate)$_{(aq)}$	-13.10				1				1					a
FeH(citrate)$^+$	-14.40		1		1				1					a
K(citrate)$^{-2}$	-1.10							1	1					a
UO$_2$(citrate)$^-$	-8.96						1		1					b
UO$_2$(Hcitrate)$_{(aq)}$	-11.40		1				1		1					b
(UO$_2$)$_2$(citrate)$_2^{-2}$	-21.30						2		2					b
U(citrate)$^+$	-12.80					1			1					c
U(citrate)$_2^{-2}$	-24.10					1			2					c
U(Hcitrate)$^{+2}$	-13.50		1			1			1					c
U(Hcitrate)$_{2(aq)}$	-26.09		2			1			2					c
U(H$_2$citrate)$^{+3}$	-14.26		2			1			1					c
U(H$_2$citrate)$_2^{+2}$	-27.61		4			1			2					c
H(NTA)$^{-2}$	-10.28		1							1				a
H$_2$(NTA)$^-$	-13.22		2							1				a
H$_3$(NTA)$_{(aq)}$	-15.22		3							1				a
H$_4$(NTA)$^+$	-16.22		4							1				a
Fe(NTA)$^-$	-10.19			1						1				a
Fe(NTA)$_2^{-4}$	-12.62			1						2				a
FeH(NTA)$_{(aq)}$	-12.29		1	1						1				a
FeOH(NTA)$^{-2}$	1.06	1	-1	1						1				a
Fe(NTA)$_{(aq)}$	-17.80				1					1				a
Fe(NTA)$_2^{-3}$	-25.90				1					2				a
FeOH(NTA)$^-$	-13.23	1	-1		1					1				a
U(NTA)$^+$	-15.16					1				1				d
U(NTA)$_2^{-2}$	-28.60					1				2				d
UO$_2$(NTA)$^-$	-8.21						1			1				e
UO$_2$H(NTA)$_{(aq)}$	-12.27		1				1			1				e
UO$_2$(NTA)OH^{-2}	-2.39	1	-1				1			1				e
H(EDTA)$^{-3}$	-10.95		1								1			a
H$_2$(EDTA)$^{-2}$	-17.22		2								1			a
H$_3$(EDTA)$^-$	-20.34		3								1			a
H$_4$(EDTA)$_{(aq)}$	-22.50		4								1			a
H$_5$(EDTA)$^+$	-24.00		5								1			a
Fe(EDTA)$^{-2}$	-16.00			1							1			a
FeH(EDTA)$^-$	-19.06		1	1							1			a
FeOH(EDTA)$^{-3}$	-6.50	1	-1	1							1			a
Fe(OH)$_2$(EDTA)$^{-4}$	4.00	2	-2	1							1			a
Fe(EDTA)$^-$	-27.70				1						1			a
FeH(EDTA)$_{(aq)}$	-29.20		1		1						1			a
FeOH(EDTA)$^{-2}$	-19.90	1	-1		1						1			a
Fe(OH)$_2$(EDTA)$^{-3}$	-9.85	2	-2		1						1			a
K(EDTA)$^{-3}$	-1.70							1			1			a
UO$_2$(EDTA)$^{-2}$	-13.70						1				1			b
(UO$_2$)$_2$(EDTA)$_{(aq)}$	-20.60						2				1			b
UO$_2$(HEDTA)$^-$	-19.32		1				1				1			b
UEDTA$_{(aq)}$	-29.50					1					1			b

	log K[a]														Ref
UO2$_{(cr)}$	-4.88	2	-4			1										f
Fe$_2$O$_{3(cr)}$	0.11	3	-6		2											g
Fe(OH)$_{3(am)}$	3.12	1.5	-3		1											g
UO$_2$(CO$_3$)$_3{}^{-4}$	-21.84						1					3				f
Fe^{+2}	-13.011				1										1	h
U^{+4}	-9.049	-2	4				1								2	h
HCO$_3{}^-$	-10.329		1												1	h

[a] Database minteq.v4.dat 85 2005-02-02 (mostly from the National Institute of Standards and Technology) (U.S. EPA, 1999; Gustafsson, 2004)
[b] Hummel et al. (2005)
[c] Bonin et al. (2008)
[d] Bonin et al. (2009)
[e] deStefano et al. (2006)
[f] Guillaumont et al. (2003)
[g] After Helgeson et al. (1978) and Majzlan et al. (2004)
[h] SNL (2007)
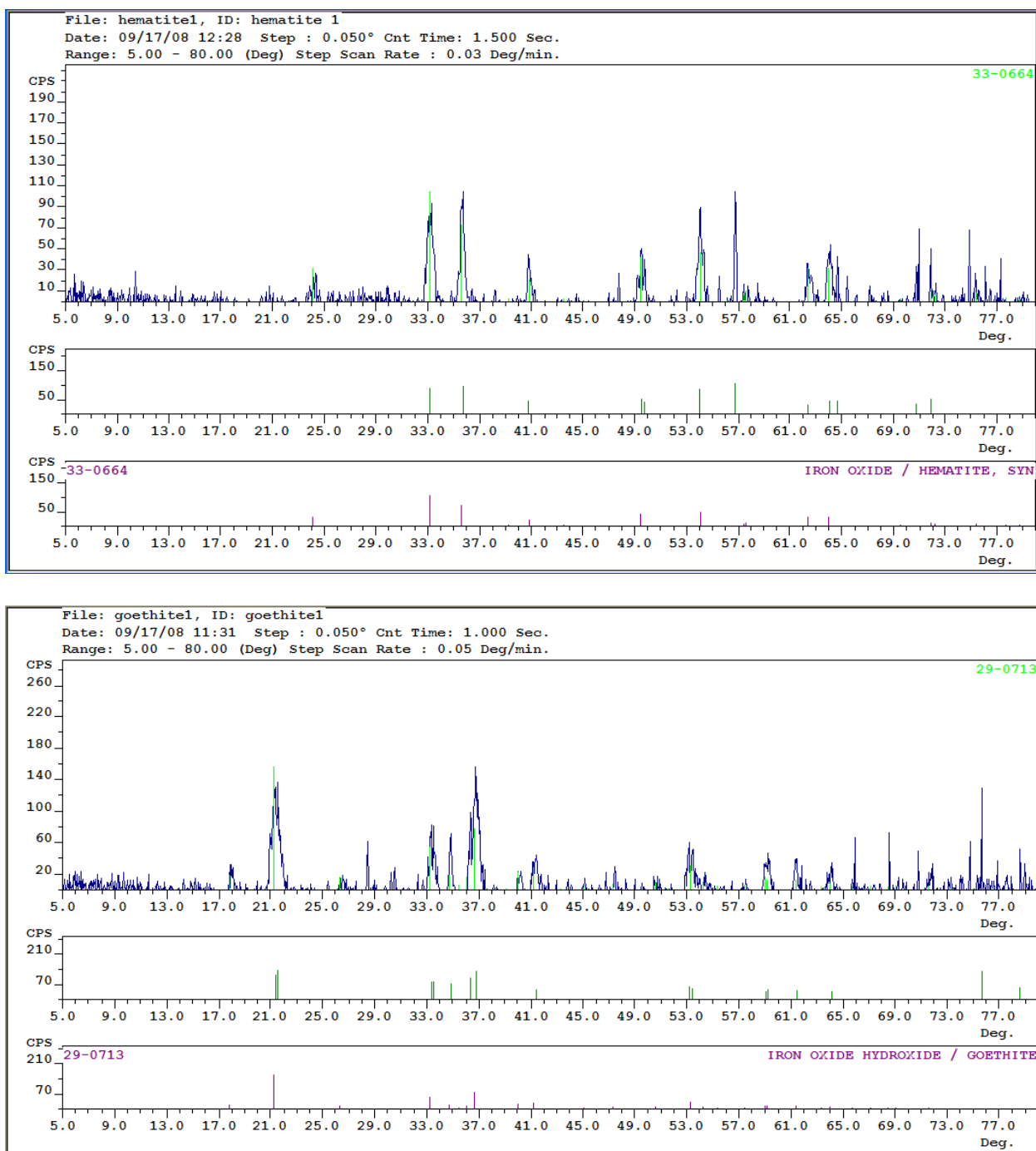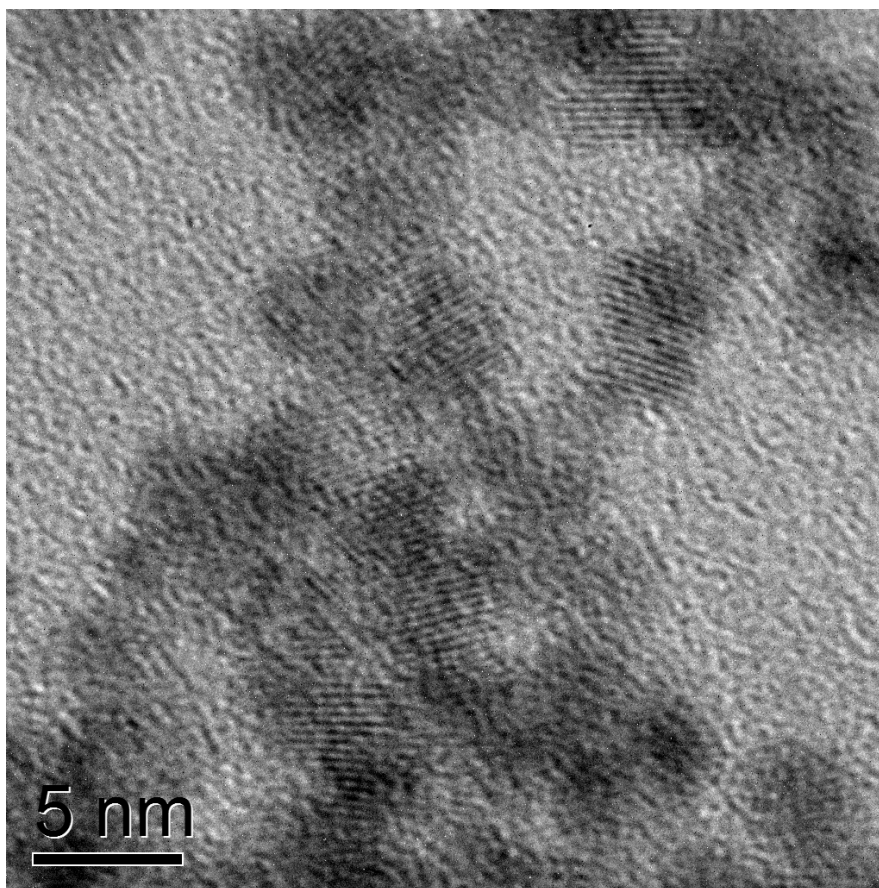
Figure S1: XRD patterns of goethite and hematite.
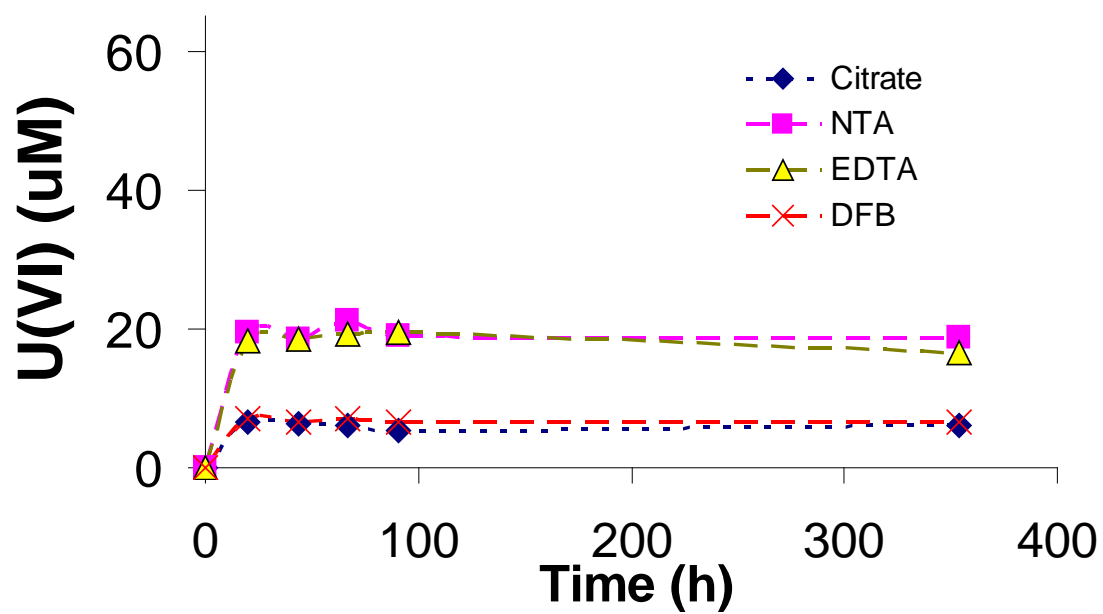
Figure S2: TEM image of biogenic UO_2.

Figure S3. Reoxidation of UO_2 by Fe(III) chloride and citrate, NTA, EDTA and DFB showing impact of a soluble Fe(III) source on U reoxidation